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INFRARED FOURIER TRANSFORM SPECTROMETRY OF GAS CHROMATOGRAPHY EFFLUENTS

Leo V. Azarraga, et al

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Athens, Georgia

January 1974

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An evaluation was made of the performance of a computerized Fourier transform infrared spectrometer for the on-line measurement of the infrared spectra of GC effluents. An optimum condition for GCIR analysis was described. Detection limits of a few nanomoles were obtained for common organic compounds. The system requires between 10 and 100 nanomoles of organic substances for qualitative identification. (Azarraga-SERL)

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INFRARED FOURIER TRANSFORM SPECTROMETRY OF GAS CHROMATOGRAPHY EFFLUENTS

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ABSTRACT

A study was made on vapor phase GC/IR analysis with the Digilab FTS-14D/IR, GC/IR, spectrophotometer in order to determine its performance. The chromatographic equipment consists of a P.E. 990 GC equipped with a 15.2 m SCOT capillary column, a flame ionization detector, a 14:1 splitter and a heated transfer line.

The maximum signal-to-noise ratio of a single scan, non-ratioed, spectrum from a GC/IR cell with 25% transmission is *ca.* 250. The detection limits for aromatic, aliphatic and other compounds with C=O functional groups are from 0.2 to 1 µg. Usable spectra may be obtained for samples as small as 2 to 5 µg. Separate spectra may be obtained for GC peaks that are resolved by twice their peak widths. Effective signal averaging for trapped samples is limited to 100 scans by trap leakage. The Every Scan Mode is most useful for programmed temperature GC/IR runs. However, a cooled detector, additional software, and data storage capacity are needed to apply this mode more effectively for GC/IR analysis.

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SECTION I
CONCLUSIONS

The optimum wave number range for GC/IR analysis is between 800 and 3500 cm^{-1}, where the signal-to-noise ratio does not vary by more than an order of magnitude. The spectra above 3500 cm^{-1} and below 800 cm^{-1} are 10 to 20 times lower in signal-to-noise ratio. The transmission of the IR cell in the low frequency region is inadequate for spectral analysis of μg quantities of eluates. This is a definite disadvantage since spectral information down to 600 cm^{-1} is important for qualitative IR identification.

No degradation of GC resolution is observed in the GC/IR system. GC peaks that are resolved by twice their half-width are also resolved in the system.

The absorbance did not increase as rapidly as expected when the GC peakwidth for a given quantity of eluate was reduced by increasing the carrier gas flow. This indicates that the eluate undergoes a considerable dilution in the GC/IR cell and that the cell's volume is greater than optimum for the spectral analysis of eluates from a capillary column. Effective signal averaging is limited to *ca.* 100 scans on a trapped eluate. The signal-to-noise ratio deteriorates when signal averaging is carried over a longer period of time because leakage from the trap continuously attenuates the concentration of the eluate. Hence, each succeeding

scan contains a progressively lower and lower signal-to-noise ratio.

The detection limit of the current system is of the order of tenths of μg or 10^{-9} moles. Reasonably good spectra of substances are obtained for quantities one order of magnitude greater than the detection limit. An increase of one order of magnitude in sensitivity would insure the practical GC/IR analysis of organic pollutants in the ppb level of concentration.

The Every Scan mode (see last paragraph p. 11) is potentially the most useful mode of GC/IR analysis. Spectral scanning of each GC peak need not be synchronized with the signal from the GC detector. Consequently optimum spectral data on the eluates can be obtained independent of the changes in the carrier gas flow during the GC run. Furthermore, the system may be operated without the GC splitter to insure the maximum quantity of eluate in the GC/IR cell. Hardware and software additions to the present system are required to utilize this mode of spectral analysis efficiently.

SECTION II
RECOMMENDATIONS

The detection limit should be improved by at least a factor of 5 so that spectra that are useful for qualitative identification may be obtained for submicrogram quantities of samples. A GC/IR cell with half the volume and twice the optical path of the current one, coupled with a high sensitivity, cooled detector to offset the loss in signal-to-noise ratio by the concurrent decrease in the cell transmission, will probably suffice.

Additional software and hardware should be provided for automatic sampling, GC/IR data collection, processing, and storage to facilitate routine GC/IR analysis and the collection of vapor phase spectra of known compounds. The latter may be used with a spectrum or interferogram correlation software to provide the system with spectral matching capabilities for unique substance identification.

The current GC/IR system should be used for pollutant identification especially where it is practicable to concentrate the components in the sample so that the volume of the sample used for GC injection contains from 5 to 10 μg of each component.

SECTION III
INTRODUCTION

Identification of organic compounds in water at concentrations as low as 1 µg/ℓ is necessary in enforcing water pollution control legislation and evaluating the environmental impact of organic pollutants. Chromatography and mass spectrometry are currently the most generally used methods for the analysis of those substances. The Environmental Protection Agency is developing a gas chromatography-mass spectrometry system and a computerized spectral matching library for organic analysis.

In general, methods of organic compound identification rely on the empirical correlation between molecular properties and the observed data. As such, ambiguity in substance identification can be expected. Confirmation by two or more independent analytical methods is preferable.

The infrared spectrum contains unique structural information on the molecule. This information when combined with those derived from other analytical methods should reduce to a high degree the uncertainties in the identification of substances.

The combination of gas chromatography and infrared spectroscopy (GC/IR system) offers considerable potential for obtaining this desired information. The infrared spectrum of a GC effluent may be obtained in two

ways: one is the on-line measurement of the IR spectrum of the eluates (GC/IR method); the other involves the trapping or isolation of the eluted substance, which is then dispersed or dissolved in an appropriate medium for IR spectral analysis. The latter process is tedious and time consuming. Losses of substances being isolated are very likely. It is, however, quite sensitive; quantities of substances of the order of 0.1 μg are sufficient for spectral analysis in most cases, and an extensive collection of standard spectra is available for qualitative identification by spectral matching.

On-line measurement of the infrared spectrum allows a real time spectral analysis of the GC effluent. In conventional GC/IR systems, the spectrum obtained is that of the substance in the gas phase. The positions and contours of the absorption bands in such a spectrum will differ, generally, from those of the same substance in the condensed phase. Qualitative identification by matching with standard spectra, which are mostly condensed phase spectra, is not a straight forward process.

The lack of an extensive collection of standard vapor phase spectra for qualitative identification purposes is, however, not a serious disadvantage in GC/IR analysis.

The simplicity and speed of the technique allow the spectral measurement in a series of compounds to be

performed without a great deal of difficulty. Solutions of known compounds suspected to include the unknown may be injected into the GC. The spectrum of each compound may be recorded under exactly the same conditions used for the unknown, and spectral matching for qualitative identification may be performed. These compounds need not be rigorously pure so long as the impurities are separable under the GC conditions used. If the known substances are also separated by the GC, a single solution containing them may be subjected to GC/IR analysis.

The spectrum of each compound can be recorded in a single GC run with a considerable savings in time and sample manipulations. Each spectrum may be stored for future reference. Furthermore, matching of the vapor phase spectra would lead to a more accurate means of identification since the absorption frequencies and intensities are free from solvent and matrix effects. The sensitivity reported for vapor phase GC/IR analysis is between 10 and 50 μg[1]. Good quality spectra were also reported for .001 and .005 μl quantities of pure liquids.[2] A recent innovation to the GC/IR technique allows for the on-line recording of spectra of GC eluates in solution.[3] A cholesteric liquid crystal film in the GC/IR cell fractionates the eluted substances from the carrier gas and enables the solution spectra of 50 μg of the eluates to be recorded on-the-fly.

This report deals with vapor phase GC/IR measurements using the Digilab FTS-14D/IR spectrophotometer with its GC/IR accessory and a Perkin-Elmer 990 GC. Its purposes are to report the experimental conditions and

instrumental operations for optimum spectral analysis and to find out what modifications or additions to the present system may be required to enhance its performance and capabilities.

In view of these objectives, only synthetic samples were used in our work. Such factors as the signal-to-noise ratio, sensitivity, optimum determination of delay times, trap leakage rates, the time dependence of the density of the eluted compound in the IR cell, and the optimum use of the various GC/IR modes for analysis were investigated.

SECTION IV
EXPERIMENTAL

INSTRUMENTATION AND FUNCTIONAL DESCRIPTION

Figure 1 is a block diagram of the experimental setup. A Digilab FTS-14D/IR spectrophotometer equipped with the Digilab GC/IR accessory and controller was connected with a Perkin-Elmer 990 Gas Chromatograph. The latter was equipped with a SCOT capillary column, a flame ionization detector, and a 14:1 splitter. The splitter was derived from a standard 50:1 splitter by constricting the output port so that an adequate signal from the FID was obtained for submicrogram quantities of the compounds injected. A Wilks heated transfer line connects the output of the splitter to the IR cell.

The IR cell is a cylindrical cavity, 6 mm in diameter and 50 mm long, bored through a heated metal block. KBr windows are sealed to each open end of the cavity. The inlet and exit ports of the cell are arranged in such a manner that the gas stream sweeps the full length of the cell. A system of valves, which can be manually or automatically actuated, allows the flow of the carrier gas to be stopped or the eluted substance to be trapped in the IR cell.

Infrared radiation is passed through the cell by means of an elipsoidal mirror located at the input side of the cell. A plane mirror reflects the IR beam from the interferometer into the ellipsoidal mirror. The IR

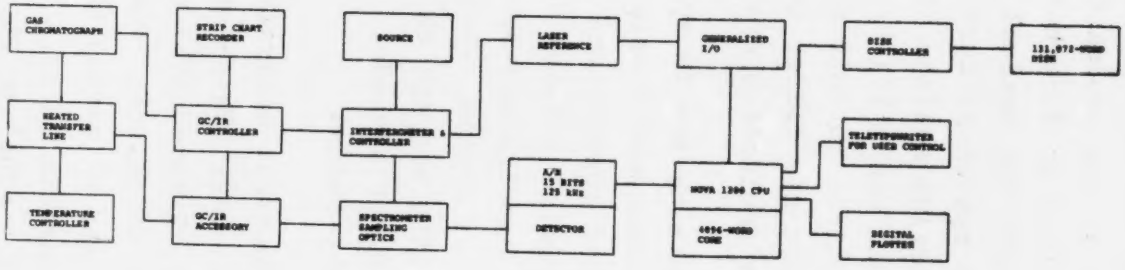

Figure 1. Block diagram of the GC/IR system

beam, after passing through the cell, is collected by another ellipsoidal mirror at the opposite end of the cell. The collected radiation is directed into a plane mirror,which reflects it into the optical system in the spectrometer. The optical system in turn directs the radiation into the triglycerine sulfate (TGS) pyroelectric detector. The cell has a 25% transmission when the high frequency optical cut-off filter is in the light path. Without the cut-off filter the cell transmits as much as 33% of the incident energy.

The Digilab FTS-14D/IR contains two IR systems. System 1 (SS1) is for infrared measurements using conventional IR procedures. Spectra with resolutions of 8, 4, 2, 1 and 0.5 cm^{-1} may be obtained with SS1. System 3 (SS3) is the GC/IR system. All spectra are obtained at a resolution of 8 cm^{-1} in this system. Data collection for both systems between 3950 and 400 cm^{-1} at this resolution is completed within 0.6 seconds. The duty cycle per scan is approximately 1 second.

Four different modes of spectral analysis of GC effluents are available in SS3. These are the On-The-Fly (FL), Every Scan (EV), Trapped (TR), and Stop-Flow (ST) modes, each of which is unique. The desired mode of operation may be selected by giving the GC mode parameter, GCM, the appropriate value. Thus, for an On-The-Fly mode, GCM is set equal to FL.

When GCM = FL, the spectrum of each GC peak is obtained. The number of scans taken for each GC peak is determined

by the length of time the signal from the FID exceeds the threshold voltage of the scan threshold sensing circuit of the GC/IR controller. The data from the scans taken are automatically coherently added (co-added) and stored in the disk. The location of the data is designated by the parameter, PKN. The storage is sequential. Thus, the data from the first peak is at PKN=1, the next at PKN=2, etc. The spectra of all the peaks in the chromatogram may be obtained by setting the parameter NPK equal to the number of GC peaks. As many as 80 spectra may be stored in the disk.

When GCM=EV, the spectrometer takes consecutive sets of scans, co-adds the data for the number of scans in the set, and stores each co-added scan sequentially until all the files are filled or the data collection is terminated by the operator. The number of scans per set is specified by the parameter, NSS.

In the trap mode, GCM=TR, a particular peak in the chromatogram may be trapped in the IR cell while the rest of the effluent is allowed to bypass it. If trapping of the nth peak is desired, the PKN parameter is set equal to that number. NPK must be set $\geq$ PKN. The number of scans taken on the trapped sample is determined by the value of NSS. The trap automatically opens after NSS scans are completed.

The Stop-Flow mode, GCM=ST, allows one to stop the flow of the carrier gas while NSS scans are taken on a GC

peak. After NSS scans are completed the Stop-Flow valve opens automatically. Spectral analysis of each peak in the chromatogram may be carried out in this manner if no degradation of GC resolution occurs. Switches are located on the GC/IR controller to allow manual scan, trap, and stop-flow operations. SS3 contains provision for automated operation with an automatic GC injector.

Except for the EV mode of operation, data must be collected at the instant when the GC component is in the IR cell. The eluted substance has to travel from the GC column to the IR cell. There is a time difference between the time the signal is received from the FID by the peak detection circuit in the GC/IR controller and the time the maximum quantity of the eluted compound is actually in the IR cell. A program, called the GC timing setup, to measure this time lag is provided in SS3. It is brought into operation by the command GCT. The parameter, MAR, is given a value equal to the per cent change in the intensity of the center burst of the interferogram due to instrumental variation. After the MAR value is set by the operators, the GCT command is executed and a strong IR absorbing compound is injected into the GC. The peak detect circuit in the GC/IR controller senses the maximum of the FID signal and counts the number of scans as the intensity of the interferogram decreases to a minimum. The number of scans is printed out by the teletype as the value of the time delay parameter, TIM. The value of TIM

remains useful so long as the carrier gas flow rate remains unchanged.

Data collection in all four modes is performed by executing the command GCS. The data stored at this stage are interferograms. The interferogram in a file specified by PKN may be plotted by setting the plot mode parameter, PLM, equal to its non-ratioed plot mode value, E, and executing the GC plot command, GCP.

The interferogram is transformed into a non-ratioed spectrum and plotted when the command to compute , GCC, is executed.

The ratioed spectrum is not stored in the system. It may be plotted by executing the command GCP when PLM is set equal to T, A, or L if a transmission, absorbance, or log absorbance plot is desired, respectively. Stored spectra in any of the sample files may be ratioed to any of the reference or background spectra in the reference file. The location of the latter is defined by the parameter, REF, which may be equated to any interger from 1 to 5. Thus, as many as five separate background spectra may be stored. A reference spectrum may be taken before or after a GC run. To collect a reference spectrum a value for REF is designated, PKN is set equal to zero, and NSR to the number of scans desired. Collection of reference interferograms is performed by executing the command GCR. Computing of the spectrum from the interferogram and plotting it in the non-ratioed mode, PLM=E, is effected

when the command GCC is executed. In SS3, stored data (interferogram or spectrum) are plotted by executing the command GCP. The value in wave numbers given for the Start-of-Plot (STP) and End-of-Plot (ENP) parameters determines the frequency range to be displayed. A list of fifteen commands containing *ca.* sixty-four parameter updates may be executed.

MATERIALS

Biphenyl, Chem Service, Inc., HP grade; mp 69.5 - 70.5°

Chloroform, Burdick & Jackson, distilled in glass

Cyclohexanone, Chem Service, Inc., HP grade; Bp 154-156°

Diethyl ethylmalonate, Chem Service, Inc., HP grade; Bp 95-97°/15 mm

Diethyl malonate, Chem Service, Inc., Purif.; Bp 198-9°

Diethyl oxalate, Chem Service, Inc., Purif.; Bp 184-6°

Dimethyl adipate, Chem Service, Inc., HP grade; mp 9-10°

Dimethyl oxalate, Chem Service, Inc., HP grade; mp 53-55°

Naphthalene, J. T. Baker Chem. Co., "Baker Analyzed," mp 80°

Tetradecane, Pfaltz & Bauer

PROCEDURES

General

The compounds were used as received without further purification. Stock solutions of each compound were made in chloroform at concentrations of 25, 20, 15, 10, and 5 µg/µl. Solutions of lower concentrations were prepared by diluting appropriate portions of the stock solutions. A multi-component solution containing the five diesters, each at a concentration of 25 µg/µl, was also prepared. In these experiments unless otherwise specified, a 1 µl injection was made using a 10 µl syringe. GC/IR analyses of solutions containing only a single solute were carried out under isothermal GC conditions. Multi-solute solutions were analyzed under GC programmed temperature.

The temperature of the GC injection ports, manifold, transfer line, and the IR cell were set at least 50° C above the column oven temperature. The spectrometer was purged with N_2 at a rate of 2.5 ℓ/min.

Determination of the Optimum Value of TIM

While the value of the time delay parameter may be obtained by the GCT program, this value although precise is likely to be erroneous. Its accuracy depends to a large extent on the accuracy of the value of MAR, which is not calculated directly in the program. The value for MAR is the best guess by the operator of the per cent change in the intensity of the interferogram due to instrumental variations.

In our work the time delay parameters were obtained in one of two different ways to eliminate this source of error. In one method the GCT program was used with MAR set to a value *ca.* 5. Acetone was injected into the GC and the center burst of the interferogram for each scan was displayed sequentially on a storage oscilloscope. The horizontal sweep was displaced slightly to the right for each scan so that a raster-type display was obtained. The number of the scan in the array giving the minimum intensity was assigned to the parameter TIM.

In the other method, the actual solution of the compound for GC/IR analysis was used. A sixteen scan background spectrum was collected using the following entry:

```
REF/1
PKN/0
NSR/16
GCR
GCC
:
```

after the reference was obtained the EV mode of operational analysis was used, i.e.,

```
GCM/EV
PKN/1
NSS/1
TIM/1
GCS
```

The solution was injected into the GC and after the solvent was eluted completely, GCS was executed. The

interferometer began to scan after the threshold voltage was exceeded. Thus, each single scan spectrum was stored sequentially on file. The value of TIM was equal to 1 plus the value of PKN containing the most intense spectrum in the file. The TIM values obtained were tested for each GC/IR mode.

Profile of the Eluted Peak in the IR Cell

Data collection identical with the GCM=EV mode for TIM determination was used to define the time dependence of the concentration of the eluted substance in the IR cell. The intensity of an absorption band in the spectrum of the compound was plotted against time. This time corresponded to the value of the PKN parameter associated with each spectrum. With NSS=1, consecutive PKN values were separated by 1 second intervals.

Trap Leakage Rate

Trap leakage was measured using both SS3 and SS1. A sixteen scan background spectrum at 8 cm^{-1} resolution was stored in file 1 in SS1. The parameters in SS1 were set to collect 16 scan spectra at 8 cm^{-1} resolution and to plot the frequency region containing a strong absorption band of the compound in the absorbance mode.

With the instrument in SS3, the solution of the compound was injected into the GC and the compound was trapped automatically. The toggle switch was manually turned on to keep the trap closed. The data collection was

aborted and the system was transferred to SS1. The SCN command was executed to get spectra of the trapped material at one minute intervals. The intensity of the absorption band was plotted as a function of time. A simpler method used later in this work employed only SS3 in the EV mode. NSS was set equal to 10 so that each spectrum represented a time period of 10 seconds. The solution of the compound was injected into the GC and after the solvent was completely eluted the GCS command was executed. Trapping of the eluate was done manually by means of the toggle switch, which operated the trap valve. The trap valve was closed after an appropriate delay time was allowed for by counting the required number of scans from the instant scanning was initiated by the signal from the FID. Data collection was allowed to continue until all 80 files were filled. A plot was made of the absorbance at a particular characteristic group frequency of the test compound *vs.* time.

Reconstruction of the Gas Chromatogram from IR Absorbance Data

Spectral data collection was essentially the same as the one used for TIM determination. GCM=EV, NSS=1, TIM=1, were the parameters used. GCS was executed and the solution of the diesters was injected into the GC. The GC conditions used were

Temperature of injection port and manifold, 250°C
Temperature program, 85° to 200°C @12°/min
Temperature of transfer line, 270°C

Temperature of IR cell, 265°C
Column, 15.24m SCOT SE30
Carrier gas flow, 9.4 ml/min of He measured at the IR cell outlet
Splitter, 14:1

Data collection was allowed to proceed until all 80 files were filled. The previous GCS command was deleted. The plot parameters were set to display C=O stretching frequency region of the spectrum in the absorbance mode and an instruction tape to compute and plot the spectrum was fed into the punch tape reader. After all the 80 spectra were plotted, another set of data was collected, computed, and plotted. The collection of the succeeding sets of data was initiated at the point in the chromatogram at which the previous set was terminated. The solution was injected into the GC for each set of 80 spectra collected. In this manner a spectrum for every one second interval in the chromatogram was obtained. Plotting the intensity of the absorption band *vs.* time gave the IR reconstructed chromatogram.

Determination of Sensitivity

The sensitivity for three modes of spectral analysis, EV, FL, TR were tested using separate solutions of biphenyl, naphthalene, tetradecane, cyclohexanone, and dimethyl adipate. The absorbance between 3100 and 2900 cm^{-1} for the first three compounds and that between 1800 and 1700 cm^{-1} for the last two were measured.

Multiple runs were made for each compound. The quantity of material injected was plotted *vs.* the GC peak area for each compound. The areas were measured with a planimeter. The corresponding plot of absorbance *vs.* GC peak area was also made. The slope of the latter was divided by the slope of the former. The result was then expressed as μg per 10^{-3} absorbance unit. This absorbance unit corresponded to an absorption of *ca.* 0.2% of the incident energy at the frequency of the absorption band being monitored.

SECTION V
RESULTS AND DISCUSSION

NOISE AND THE OPTIMUM REGION FOR SPECTRAL ANALYSIS

A single scan non-ratioed background spectrum from the GC/IR cell is shown in Fig. 2. The spectrum intensity is maximum at 2036 cm^{-1}. The cut-off frequencies are at 450 and 3900 cm^{-1}. Below 750 cm^{-1} and above 3500 cm^{-1}, the energy is less than 10% and 20%, respectively, of the energy in the spectrum at 2036 cm^{-1}. Figures 3a, b and c show the region between 2020 and 2070 cm^{-1} with the abscissa expanded 8 times. In this figure, a is plotted without ordinate expansion; b is plotted at 50X ordinate expansion and c is a superposition of three separate single-scan spectra. In c, the noise is seen as a variation in the intensity of each corresponding peak in the superposed spectra. On the average this amounts to 20% of the intensity at 50X ordinate expansion. Thus the signal-to-noise ratio at 2036 cm^{-1} is *ca.* 250. This represents the maximum signal-to-noise ratio that can be expected from a single scan non-ratioed spectrum.

The relative noise level between 500 and 3800 cm^{-1} is shown in Fig. 4. Trace a is the ratio of a pair of single-scan background spectra; b, c, and d are those of 16-, 256- and 1024-scans spectra. All are plotted in the transmission mode without ordinate scale expansion. In a, the noise level below 800 cm^{-1} is approximately twice the noise level above 3500 cm^{-1} and

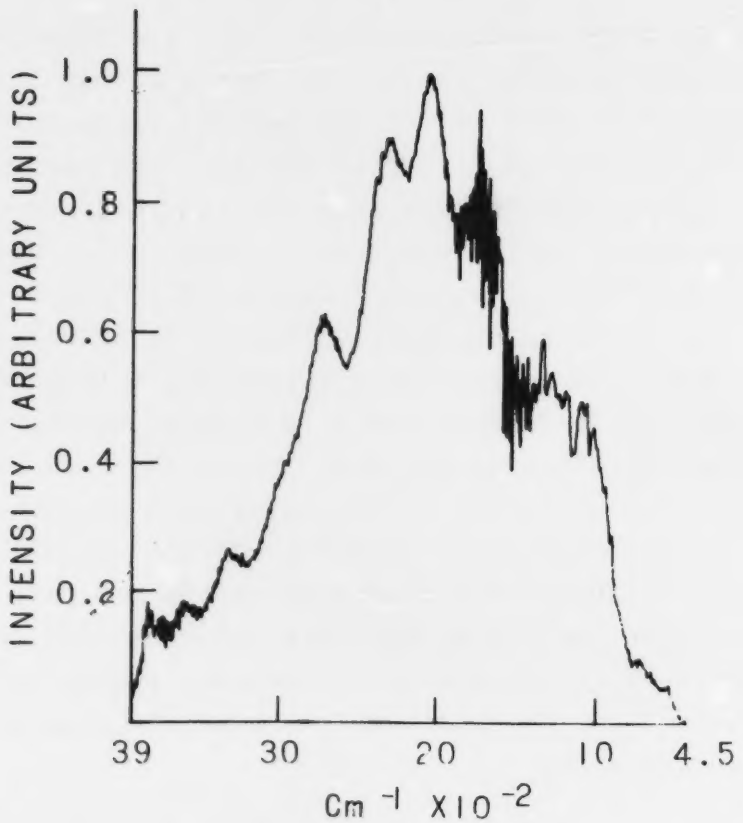

Figure 2. Non-ratioed single scan background spectrum

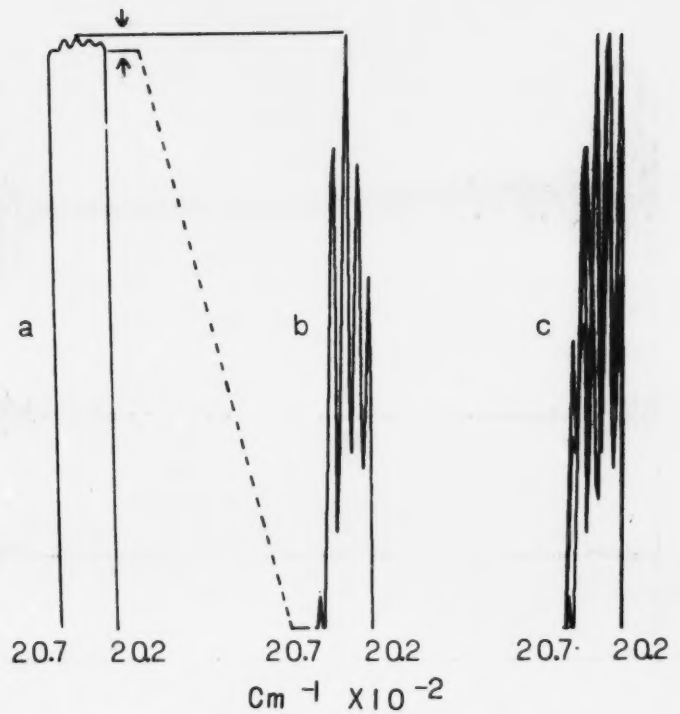

Figure 3. (a) The region of maximum intensity of the spectrum in Fig. 2 plotted at 8X abscissa expansion without ordinate expansion

(b) 50X Ordinate expansion of the portion of the spectrum shown in (a)

(c) A superposition of three single scan spectra in the same region under the same scale expansion as in (b)

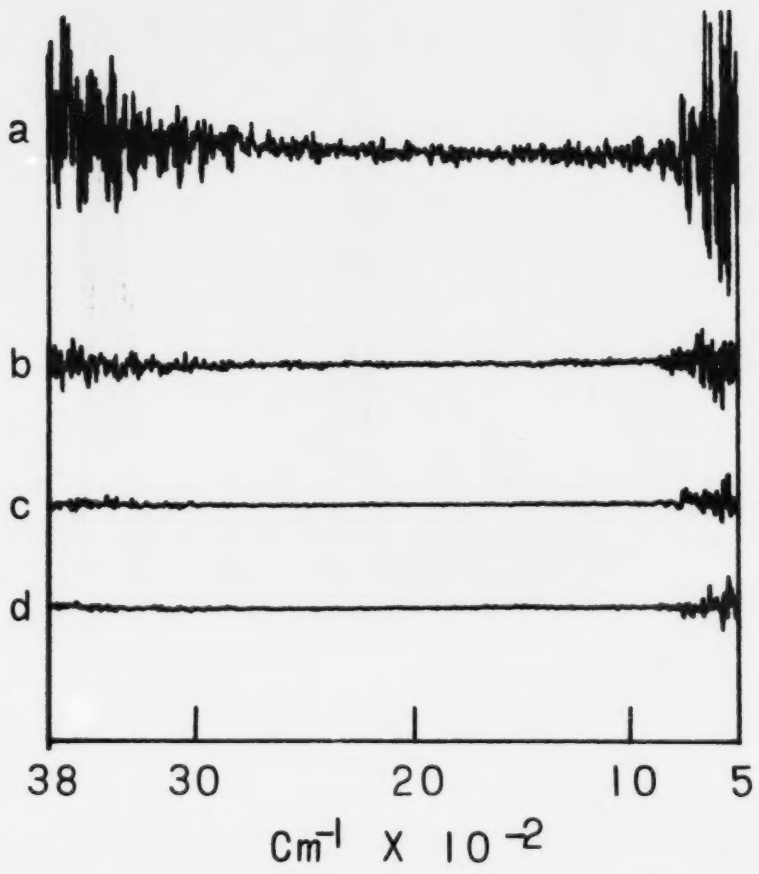

Figure 4. Transmission baseline using equal number of scans for background and sample between 500 and 3800 cm-1

almost 20 times that of the noise level between 800 and 3500 cm^{-1}. This result is in accordance with the energy distribution in the spectrum in Fig. 2.

The effect of signal averaging on noise can also be seen in Fig. 4, especially at the region below 800 cm^{-1}. In this region the ratio of the peak-to-peak noise level in traces a, b, c, and d are approximately 20:4:2:1. The relative noise level in the spectrum between 800 and 3500 cm^{-1} for these same traces is also shown in Fig. 5. Trace a is plotted without ordinate expansion, while traces b, c, and d are plotted with 10X ordinate expansion. The relative noise levels in this region for the four traces are 10:4:1.5:1. The noise level changes by no more than a factor of 10 throughout this spectral range; this region, therefore, is the optimum range for GC/IR analysis and spectral sensitivity tests.

The advantage of using a reference background spectrum containing a large number of scans is depicted in Fig. 6. Curves a, b, and c are the transmission base lines for single, 16- and 256- scans spectra ratioed to a 1024-scan background spectrum respectively. Curve d is exactly the same as d in Fig. 4. Improvement in the noise level can be readily seen when corresponding traces are compared in Figures 4 and 6. The noise level in Fig. 6a, b, and c is *ca.* 3/4 to 1/2 that of the corresponding traces in Fig. 4. This gain is due to the high signal-to-noise ratio in the reference spectrum, which theoretically should be 32 times that of a single-scan spectrum.[4] The noise in curves a and b in Fig. 6

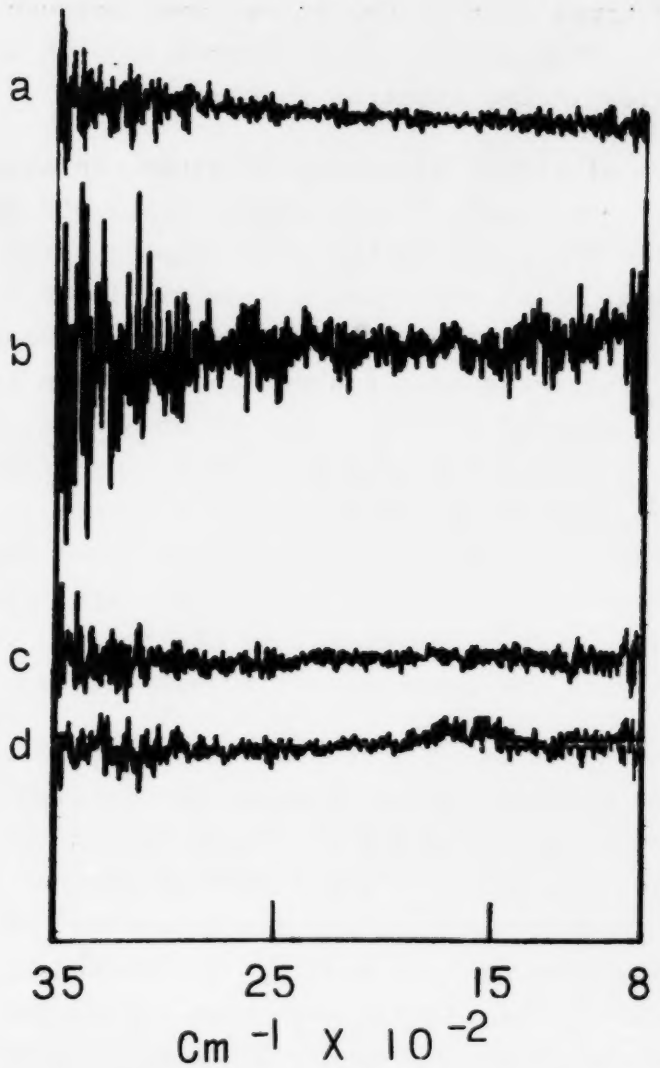

Figure 5. The noise level on the transmission baselines in Fig. 4 between 800 and 3800 cm-1. (a) no ordinate expansion, (b), (c) and (d) 10X ordinate expansion.

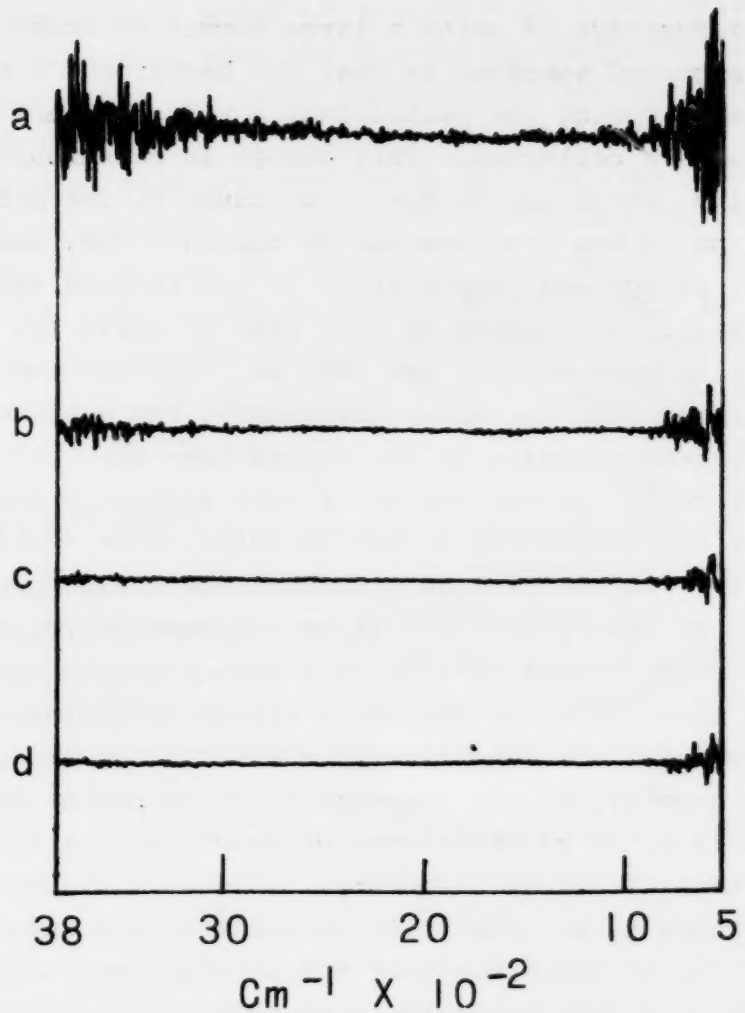

Figure 6. Transmission baselines using a 1024-scan background spectrum. NSS for a, b, c,and d are 1, 16, 256,and 1024 respectively.

is due mostly to the poor signal-to-noise ratio in the 1- and 16-scan spectra.

One disadvantage of using a large number of scans for the background spectrum is that the background intensity may change during the period that a reference and sample spectrum are collected. This change in background intensity, which may be due to a change in the purged condition in the spectrometer or column bleed, results in poor background compensation in the ratioed spectrum. It is easily noticeable in d of Fig. 5, where the water absorption between 1300 and 1800 cm^{-1} was not completely compensated for. As noted previously, the maximum signal-to-noise ratio in the single beam spectrum is 250 at 2036 cm^{-1}. If the energy at this frequency were reduced 250 times, the signal-to-noise ratio would be unity. In the ratioed spectrum this would correspond to an absorption of 0.4% of incident energy or 1.7×10^{-3} absorbance units. To obtain a common measure of the sensitivity of the GC/IR system to different types of compounds, the sensitivity is arbitrarily expressed as the quantity of the compound in µg or number of moles that will yield an absorbance of 1×10^{-3} at the selected characteristic group frequency. This unit of absorbance corresponds to an absorption of 0.23% of the incident energy and is therefore only 56% of the absorption for a unity signal-to-noise ratio at 2036 cm^{-1}. Furthermore, the noise level in the region between 800 and 3500 cm^{-1} varies by less than a factor of 10. The unit of sensitivity adopted in this work may consequently be no more than 20X greater than the true value of the sensitivity of the system for a specific compound on the basis of signal-to-noise ratio of unity.

In Fourier transform spectroscopy the criterion for detectability based on a signal-to-noise ratio of unity is valid only when the absorption bandwidth is much larger than the noise bandwidth in the spectrum. When the absorption band is weak and its halfwidth is narrower than the resolution setting used for spectral measurement, it is difficult to distinguish the noise from the signal for a signal-to-noise ratio of 1. This is because the noise bandwidth will always be greater than the absorption bandwidth. A better criterion for detectability in this case would probably be a signal-to-noise ratio of 2.[5]

GC/IR ANALYSIS

Optimization of GC/IR analysis depends essentially on finding the proper conditions for obtaining the most intense absorption spectrum for a given quantity of eluate. Two general requirements are (1) adequate purging of the spectrometer to remove as much as possible the CO_2 and water vapor from the optical path, and (2) maintaining a sufficiently high temperature throughout the path transversed by the eluate to prevent condensation. Purging with N_2 boiled off from a liquid nitrogen tank at a rate of 2.5 ℓ/min is sufficient for this purpose, although the absorption intensity due to water decreases continuously throughout an 8 hour period at this purge rate. This change, however, is relatively slow. One hour after purging is initiated, adequate compensation for H_2O absorption in the ratioed spectrum is obtained

when the sample and background spectra are collected within 15 to 30 minutes of each other. Collection of a background spectrum just before a GC/IR run proves in most cases sufficient to insure adequate background compensation. Heating the injection port, manifold, transfer lines, and IR cell to at least 50^{o} above the GC column temperature is adequate to prevent condensation.

With these conditions established, specific factors that may affect the intensity of the spectrum were investigated. Figure 7 is a time delay calibration curve for the SCOT capillary column. The time delay decreases monotonically with increasing carrier gas flow. The time delay calibration curve, which in this case was obtained with GCM=EV, may be used directly for GCM=FL but not for GCM=TR. Observations during the course of these experiments show that the optimum value of TIM for the trap mode is 1 to 3 units less than that for the GCM=FL. For sharp GC peaks (halfwidth less than 10 sec.) this difference is between 1 to 2, and for broader peaks it may be as much as 3.

From Fig. 7 one may obtain also the upper limit of carrier gas flow rate for which automatic trapping of the eluate in the IR cell is practicable in the present configuration of the system. For example, a TIM=1 for GCM=TR will correspond to a TIM=2 or 3 for GCM=FL. These correspond to flow rates between 17 to 24 ml/min. Since the minimum value of TIM for all GC/IR modes is 1 (TIM=0 is not allowed) the practical upper limit of the flow rate for trapping the eluate is *ca.* 24 ml/min.

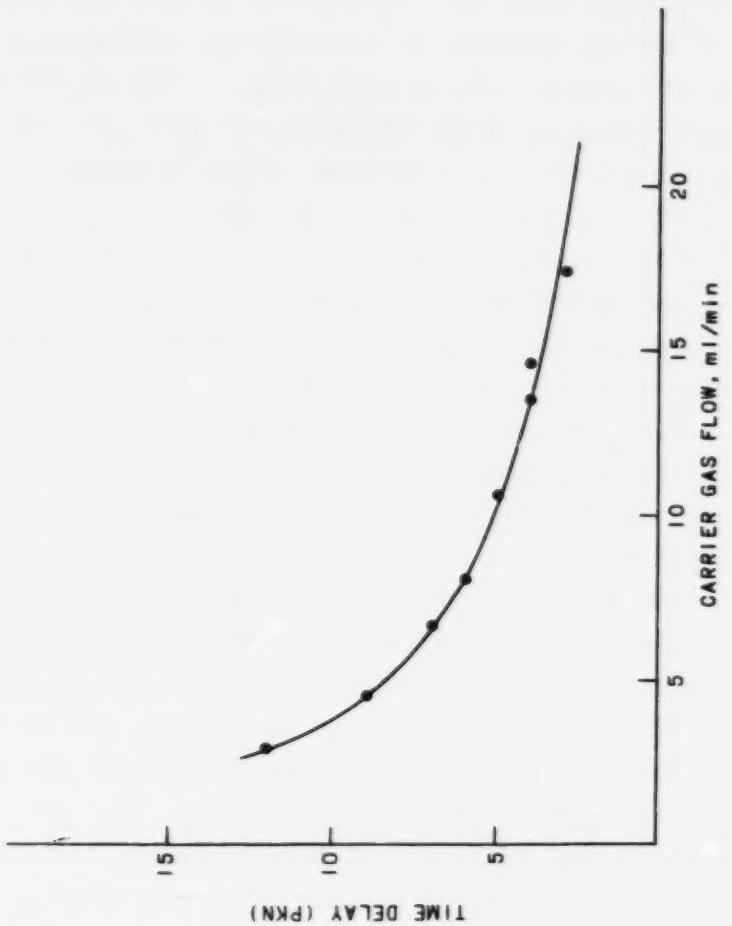

Figure 7. Time delay calibration curve showing an inverse relation between flow rate and the values of the time delay parameter

During the transit of the eluted compounds between the column and the GC/IR cell, separation of the components may deteriorate because significant change in the distribution of the eluate in the carrier gas occurs or the transit time of the eluate through the GC/IR cell is very large compared with the peak to peak separation of the eluates in the chromatogram. Fig. 8 shows the GC/IR "resolution". Curves a and b are the respective plots of the transit time of the eluted peak through the IR cell and the width of the GC peak *vs.* flow rate. The transit time is the width of the peak at half the maximum absorbance during transit of the eluate. Such a plot is shown in Fig. 9a. The corresponding GC peak is shown in Fig. 9b. It is evident from Fig. 8 that the peak to peak resolution of the GC/IR system improves with increasing carrier gas flow rate. At a flow rate of 3 ml/min the transit time is twice the GC peak width. This is reduced to a factor of 1.6 at 16 ml/min. We concluded that GC peaks resolved by twice their peak width in the chromatogram should also be resolved in the GC/IR system. There is no visible significant difference between the general shapes of the two curves a and b in Fig. 9. We further concluded that the GC resolution is not significantly degraded during the transit of the eluate to the IR cell.

The relation between GC/IR absorption intensity (curve b) and GC peak width (curve a) is shown in Fig. 10. A threefold decrease in the GC peak width results in less than 6% increase in the IR absorption intensity over a

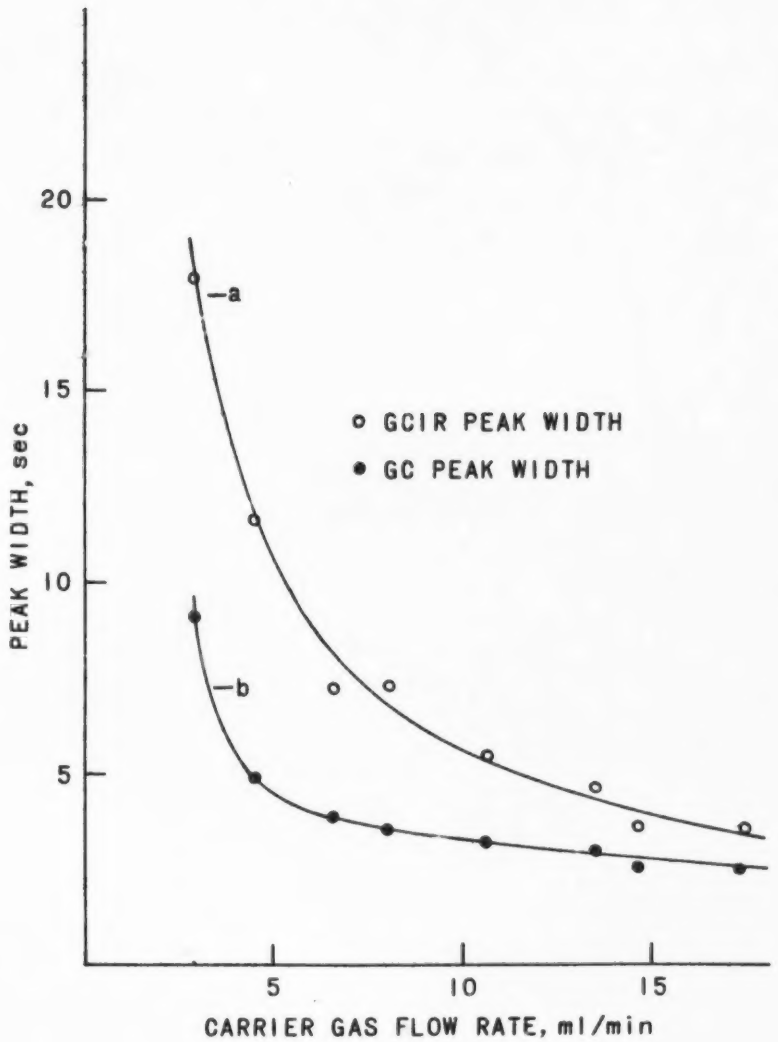

Figure 8. Plot of (a) GC peak transit time in the IR cell and

(b) GC peak width *vs.* flow rate

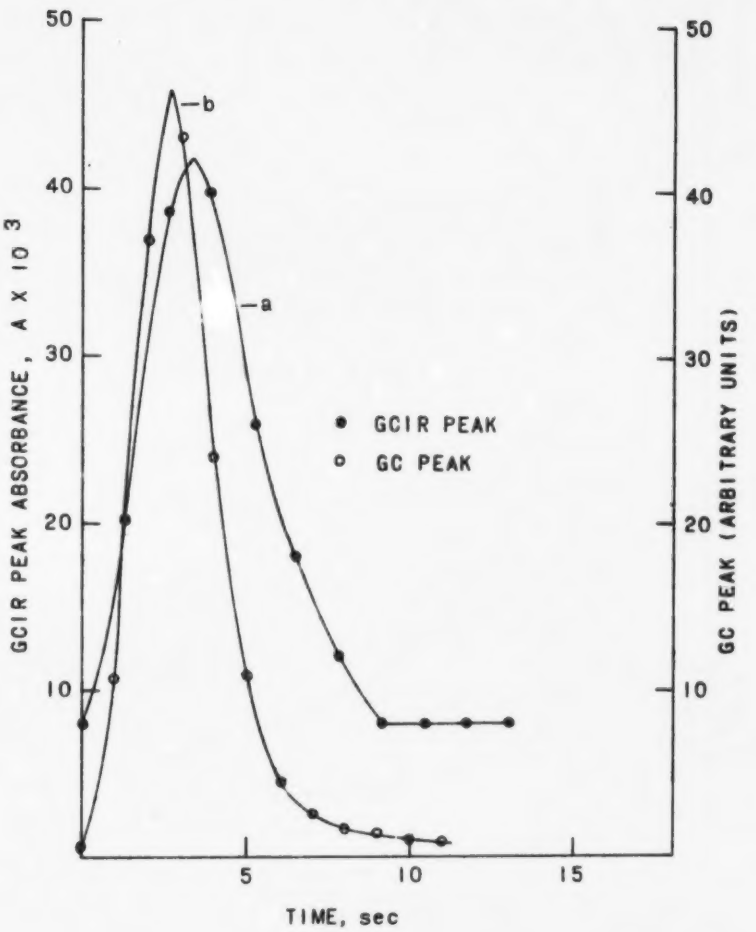

Figure 9. (a) Concentration profile of the eluate in the IR cell and

(b) Mass profile of the same eluate from the chromatograph. Carrier gas flow rate: 17 ml/min.

four fold increase in the flow rate for the present system. Since capillary columns deteriorate rather rapidly at high flow rates and since no substantial gain in GC/IR sensitivity is obtained under this condition, the flow rate optimum for GC resolution should also be optimum for GC/IR analysis.

Signal averaging is best performed by trapping the eluate, i.e., by using GCM=TR mode. The trap leakage limits the length of time for effective signal averaging. Fig. 11 shows the decrease of absorbance with time for a trapped GC eluate. The absorbance remains practically constant for 100 seconds after the trap closes and then decreases rather sharply for a period of 100 seconds. Thereafter, it decreases slowly at an approximate rate of 2.7×10^{-5} absorbance units/sec. The best period for signal averaging, therefore, is within 100 seconds after the compound is trapped. About 100 scans can be taken during this time and an improvement of 10 times the signal-to-noise ratio of a single scan spectrum may be expected.

Fig. 12 shows the effect of the number of scans on the signal-to-noise ratio at the C=O stretching region for a trapped cyclohexanone eluate. The signal-to-noise ratio increases linearly with the square root of the number of scans for NSS 100. It drops sharply for 100 NSS$\leq$256, and somewhat slowly for NSS$\leq$256. This

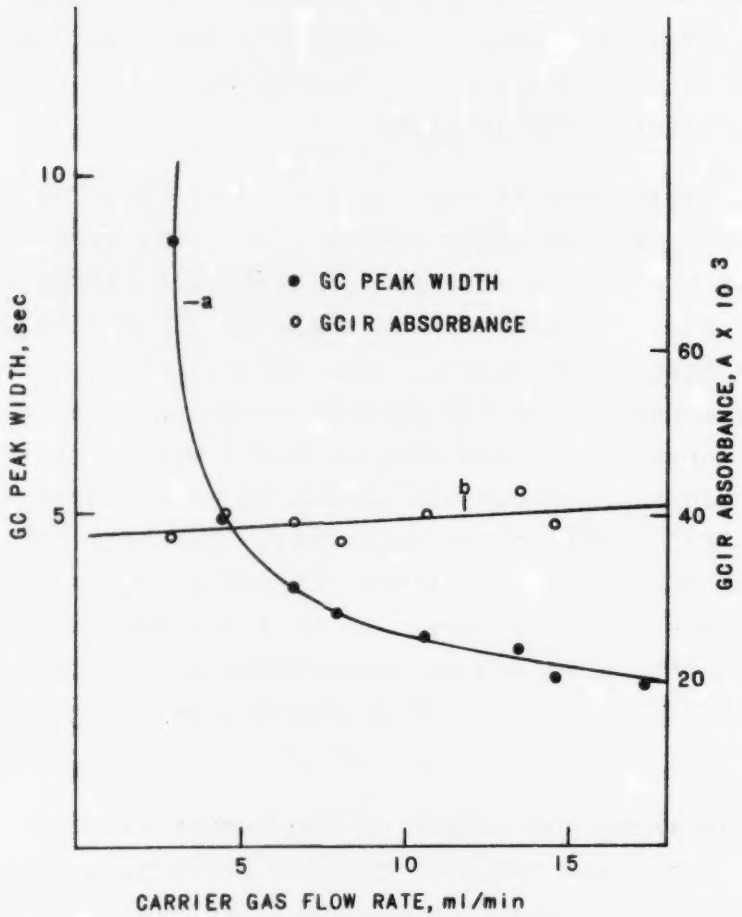

Figure 10. Plot of (a) GC peak width *vs.* flow rate and (b) Absorbance

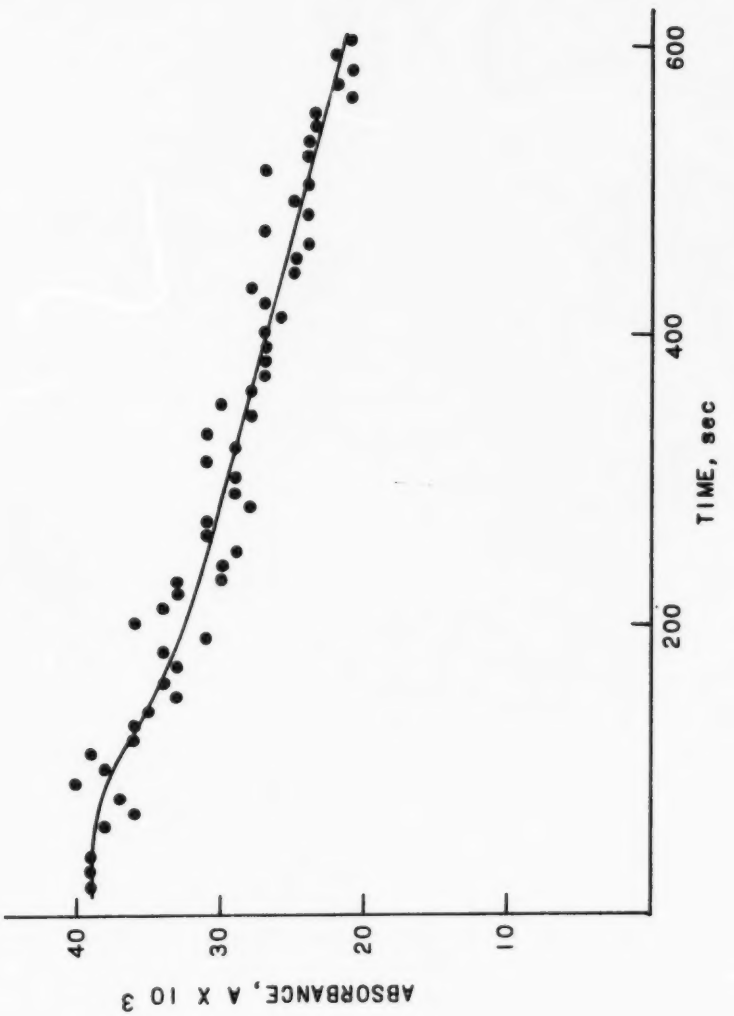

Figure 11. Plot of absorbance *vs.* time for a trapped, 5 µg, naphthalene eluate

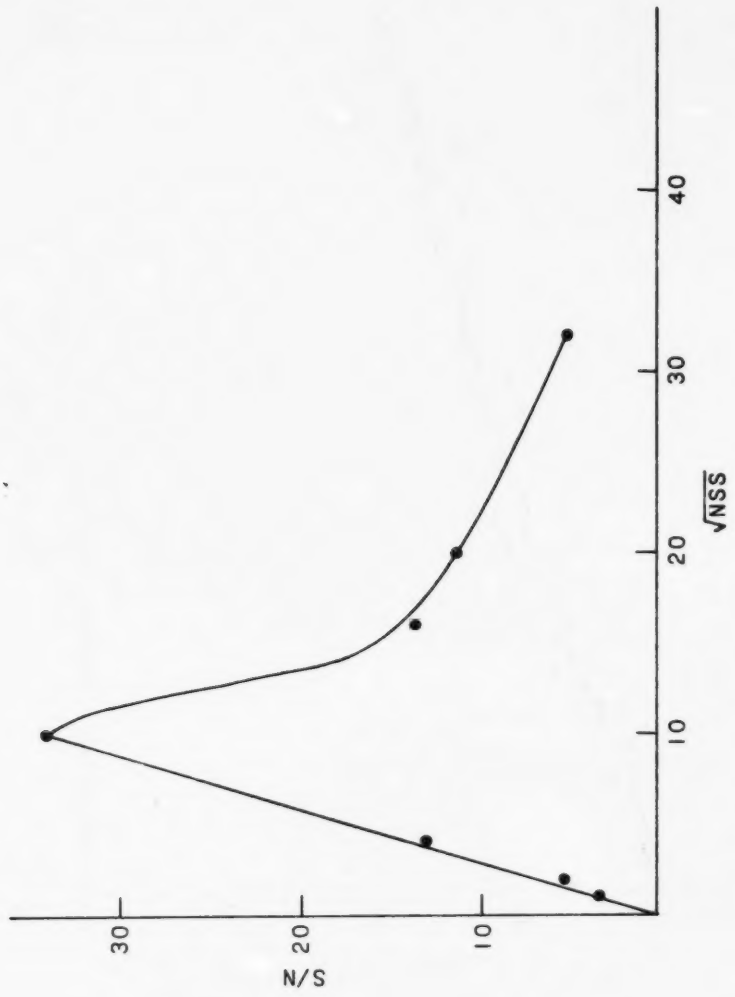

Figure 12. The signal-to-noise ratio plotted as a function of the square root of NSS for a trapped 5 µg cyclohexanone eluate

behavior correlates very well with the curve in Fig. 11. Signal averaging within the period of time when the density of the trapped eluate in the IR cell remains constant results in a gain in signal-to-noise ratio that varies directly with the square root of the number of scans. No further gain in S/N is realized by signal averaging over longer periods. In fact, if the time for signal averaging includes the period when the density of the trapped eluate is decreasing because of leakage from the trap, the signal to noise ratio of the resulting spectrum decreases. This is to be expected since the signal intensity is directly proportional to the absorbance, and, as previously mentioned, the noise is independent of the signal intensity, while signal averaging is apparently made over non-weighted single scan spectra. The maximum signal-to-noise ratio in this particular case is 34 (See Table 1) and, on the basis of S/N=1, the absolute detection limit of the instrument for cyclohexanone is 0.2 μg or 1.6×10^{-9} moles. The previous discussion on the adapted generalized expression for the detection limits ($\mu g/10^{-3} A$) does not apply to this particular case since the value of the detection limit for cyclohexanone is based directly on the optimum signal-to-noise ratio at the C=O stretching frequency for the compound.

The detection limits for other compounds are shown in Table 2. Figs. 13a-e and 14a-e are the least-squares-fitted- plots of concentration of solutions and of the absorbance at the selected group frequencies *vs*. GC

Table 1. SIGNAL TO NOISE RATIO AT THE C=O STRETCHING FREQUENCY FOR TRAPPED SAMPLES OF CYCLOHEXANONE

NSS(=NSR)	Absorbance (10^{-3}A)	S/N
4	22	5.3
16	19	13.0
100	19	34.0
256	12	13.7
400	11	11.5
1024	5	4.6

Table 2. DETECTION LIMITS FOR A NUMBER OF ORGANIC COMPOUNDS

Compounds	dm/ds μg/Unit Area	dA/ds 10^{-3}A/Unit Area	Detection Limits μg/10^{-3}A(Nano-moles/10^{-3}A)	
Biphenyl	22.5	31	0.7	(4.5)
Cyclohexanone	10.7	41	0.3	(3.1)
Dimethyl Adipate	17.0	70	0.2	(1.1)
Naphthalene	22.3	33	0.7	(5.5)
Tetradecane	22.9	16	1.4	(7.0)

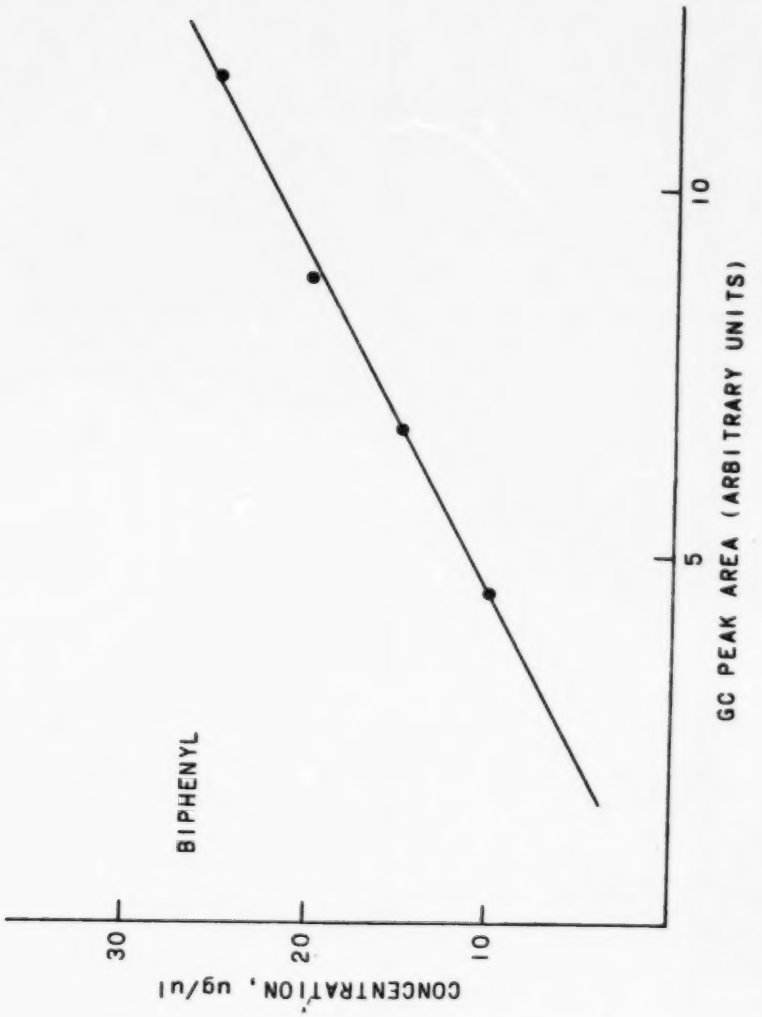

Figure 13. Plot of concentration *vs.* GC peak area
(a) Biphenyl

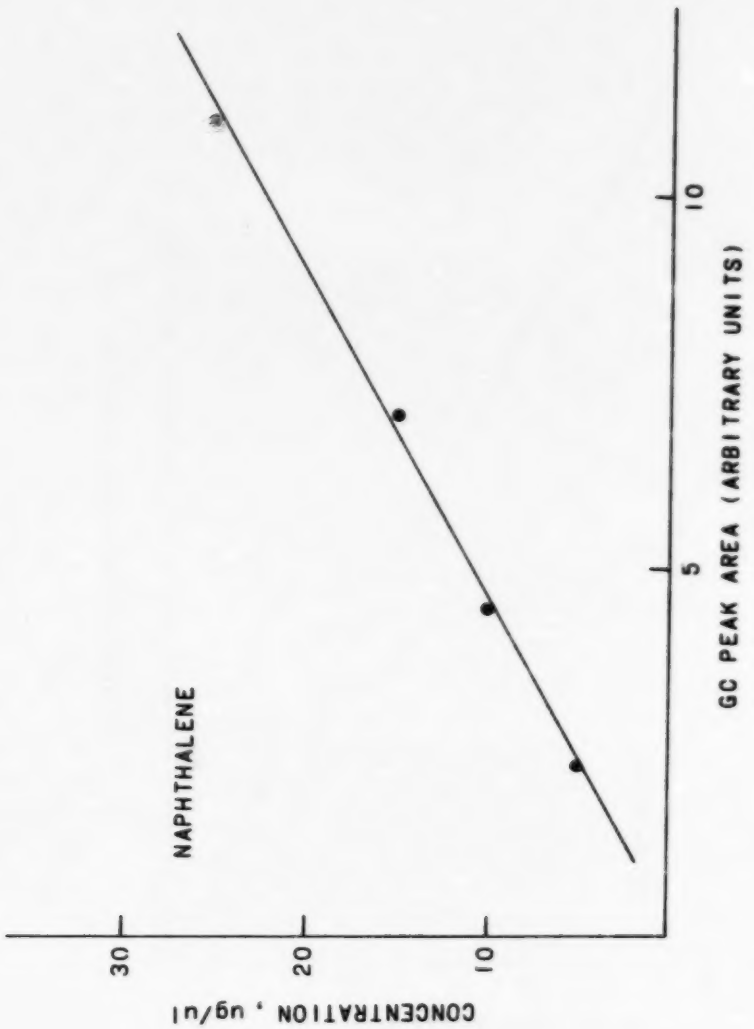

Figure 13. Plot of concentration *vs.* GC peak area
(b) Naphthalene

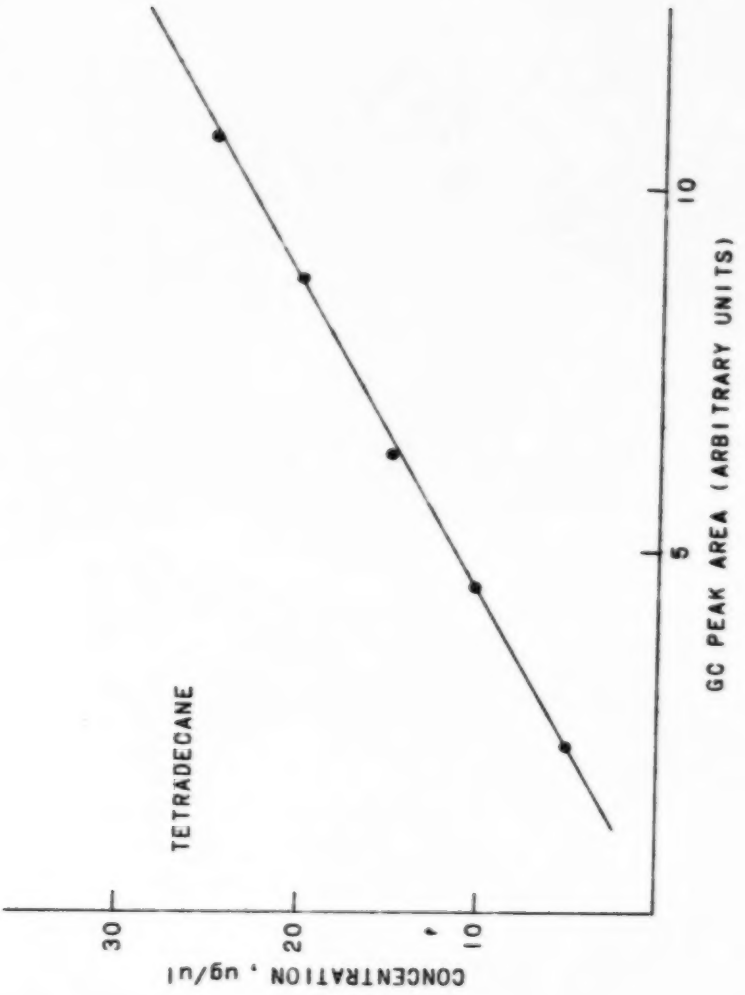

Figure 13. Plot of concentration *vs.* GC peak area
(c) Tetradecane

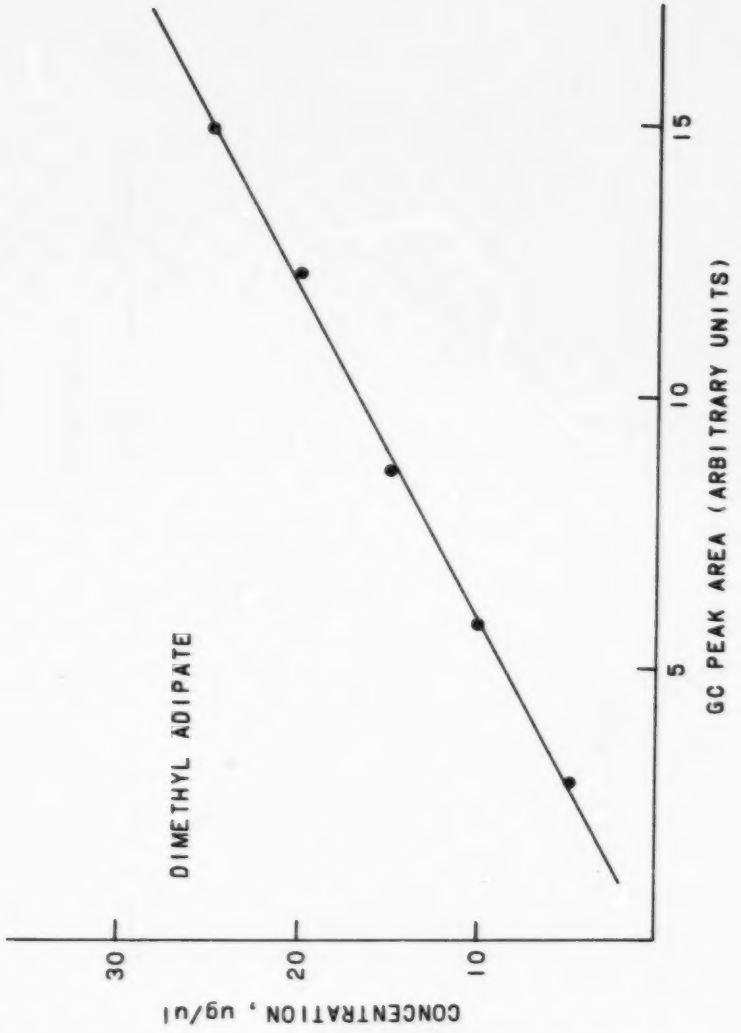

Figure 13. Plot of concentration *vs.* GC peak area
(d) Dimethyl adipate

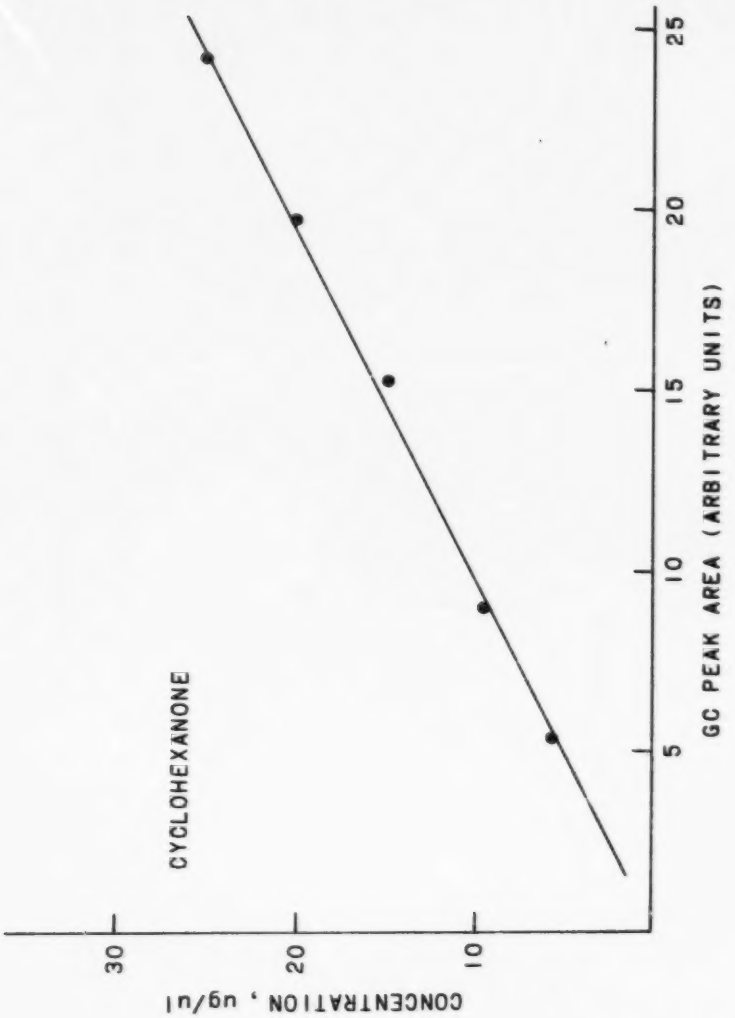

Figure 13. Plot of concentration *vs.* GC peak area
(e) Cyclohexanone

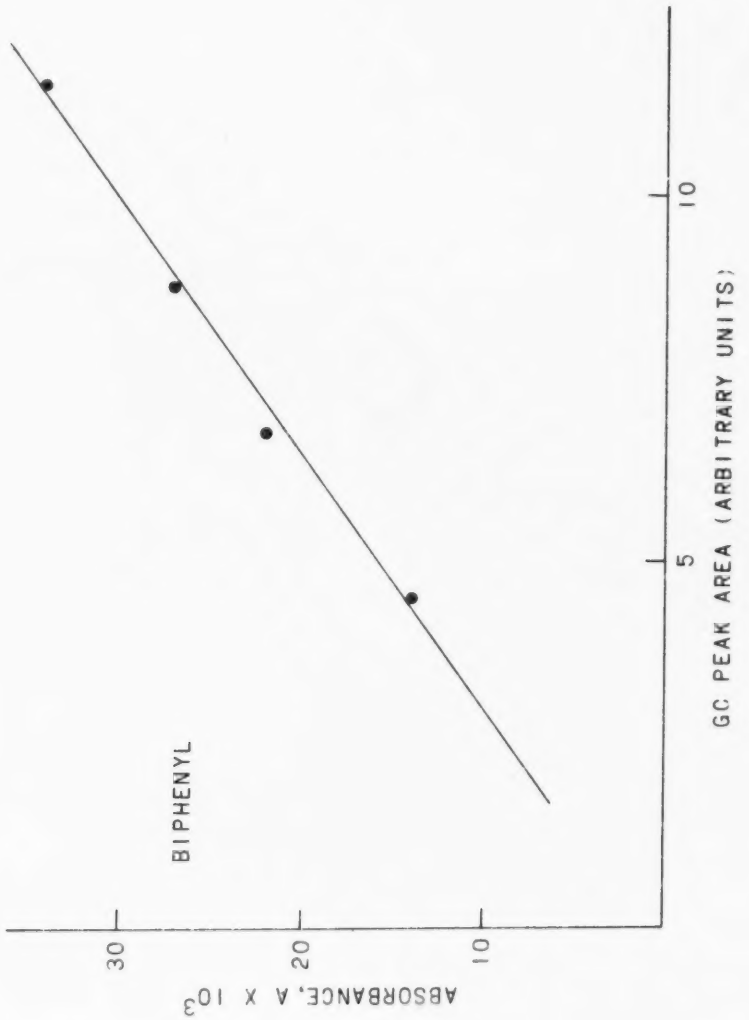

Figure 14. Plot of absorbance *vs.* GC peak area
(a) Biphenyl

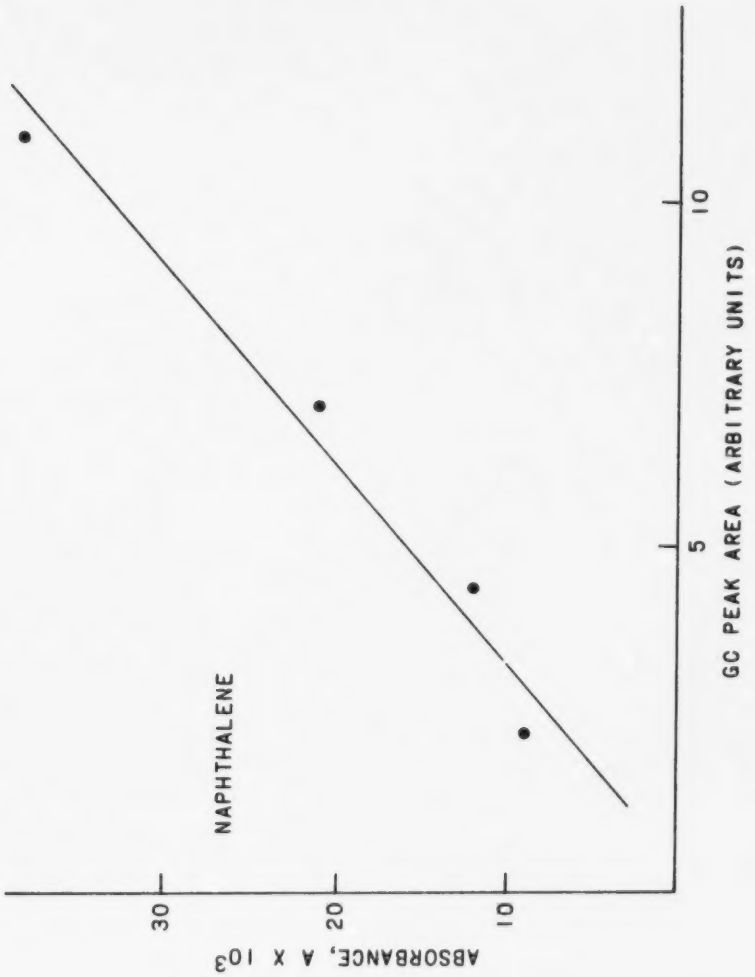

Figure 14. Plot of absorbance *vs.* GC peak area
(b) Naphthalene

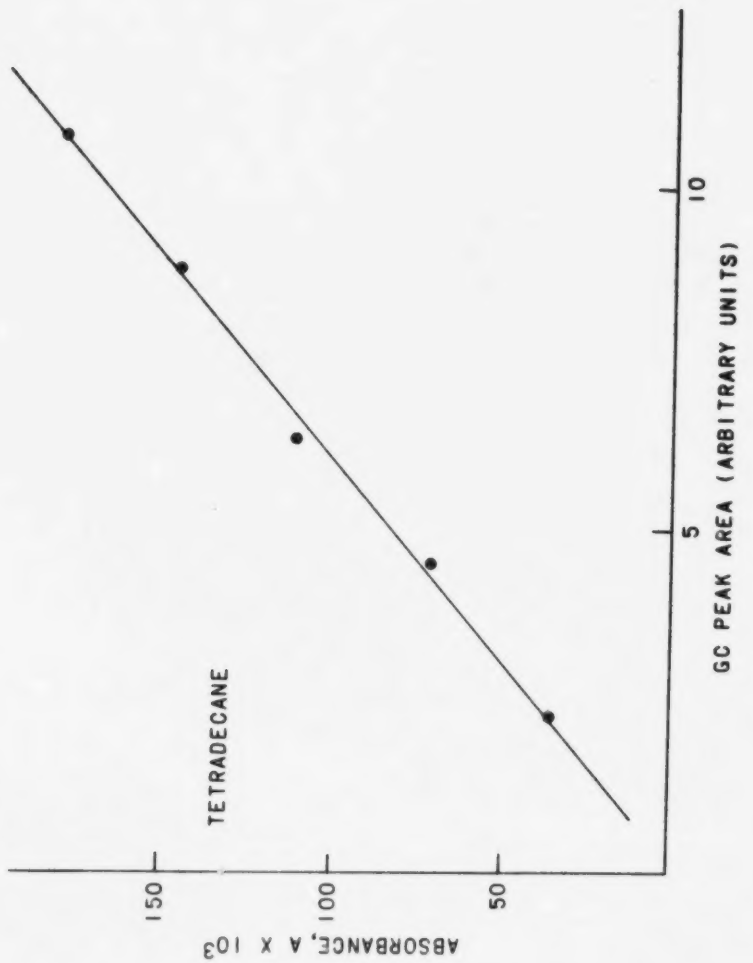

Figure 14. Plot of absorbance *vs.* GC peak area
(c) Tetradecane

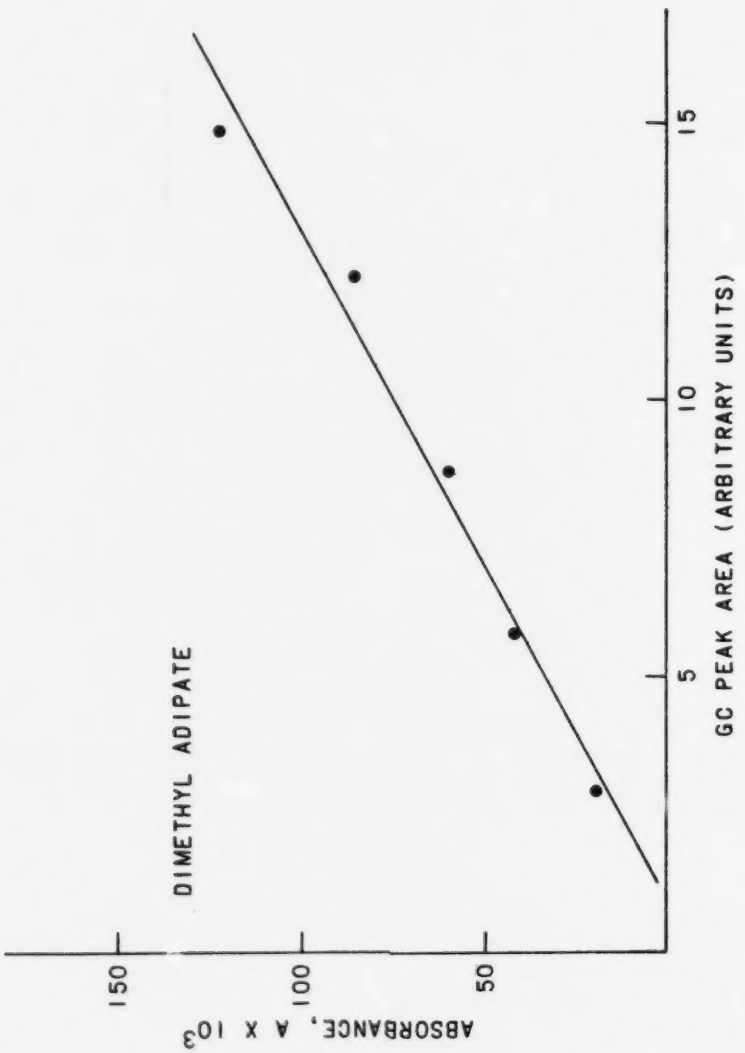

Figure 14. Plot of absorbance *vs.* GC peak area
(d) Dimethyl adipate

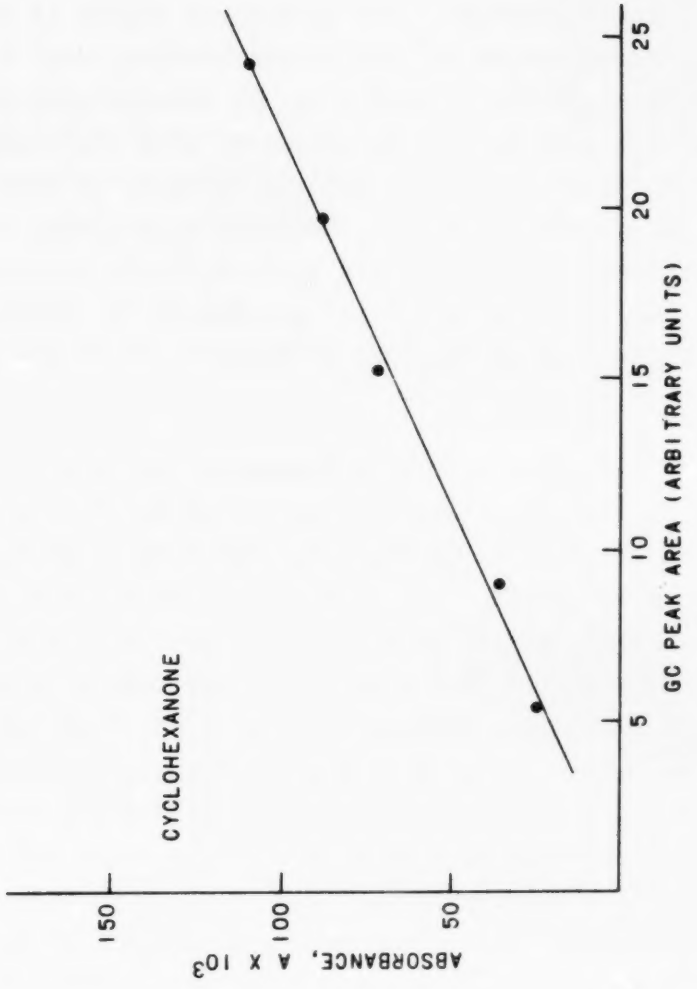

Figure 14. Plot of absorbance *vs.* GC peak area
(e) Cyclohexanone

peak area, respectively. The values in Table II were calculated from slopes of the corresponding curves in these figures. It is interesting to compare the detection limit for cyclohexanone obtained with that described in the previous paragraph. The difference is less than a factor of 2. Furthermore, the detection limit for dimethyl adipate is comparable with that for cyclohexanone. On this basis it is reasonable to conclude that the unit adopted for the detection limit for the instrument is valid.

The detection limits for cyclohexanone for the different GC/IR modes, also shown in Table 3, are practically identical. Programmed temperature conditions are almost a necessity to achieve both speed and resolution in the GC analysis of a multicomponent sample. However, the carrier gas flow often decreases as the temperature increases during the run. As shown in Fig. 7, the time delay parameter is sensitive to changes in carrier gas flow rate. If GC/IR analysis with GCM=FL is used, the synchrony between spectral scanning and the elution of the components into the IR cell deteriorates progressively with each succeeding GC peak. If the change in carrier gas flow rate does not produce a change in the delay time by more than 1/2 of the transit time of the eluate through the IR cell, it should be possible to record a spectrum of each eluate in the chromatogram. The spectra, however, will not have the optimum intensity and signal-to-noise ratio. With greater change in the flow rates, it is possible to miss the spectrum of the eluates after the first few peaks in the chromatogram.

Table 3. DETECTION LIMITS FOR CYCLOHEXANONE AT THE C=O STRETCHING FREQUENCY FOR THE DIFFERENT GC/IR MODES

GCM	NSS	NSR	Detection Limits [µg/10^{-3}A (Nano-moles/10^{-3}A)]
EV	1	16	0.2 (2.0)
FL	-	16	0.2 (2.0)
TR	16	16	0.3 (3.1)
TR	100	100	0.3 (3.1)

The Every Scan mode is potentially most suited to programmed temperature GC/IR analysis. A spectrum may be taken and stored as often as every second during the GC run. Recording of the spectrum of every GC peak is virtually assured under normal GC conditions. Fig. 15a is a reconstruction of a chromatogram from the IR absorbance data obtained with the Every Scan Mode. The corresponding chromatogram is shown in Fig. 15b. The single scan spectra, one for each eluate, plotted in the absorbance mode are shown in Fig. 16a-g. These results show the effectiveness of the chromatogram reproduction from the GC/IR absorbance data and the quality of the spectra obtained without the benefit of signal averaging.

Both software and hardware modifications will be needed in order to use the Every Scan Mode more effectively. The signal-to-noise ratio in a single scan spectrum is much too low for recording usable spectra of compounds in the µg range. Weighted co-adding of the interferograms taken during the transit of the eluate through the IR cell will be needed to optimize the signal-to-noise ratio of the spectrum. In the current system this can only be done manually. Note that in Fig. 15a, the number of spectra or interferograms needed to reconstruct a chromatogram from a single GC run far exceeds the present storage capacity of the disk. Additional data storage capacity is required for an uninterrupted data collection from one or more GC runs. The quantity of eluate for GC/IR analysis can be optimized if the GC splitter is removed and the full GC effluent is relayed to the IR cell. In this configuration a means of

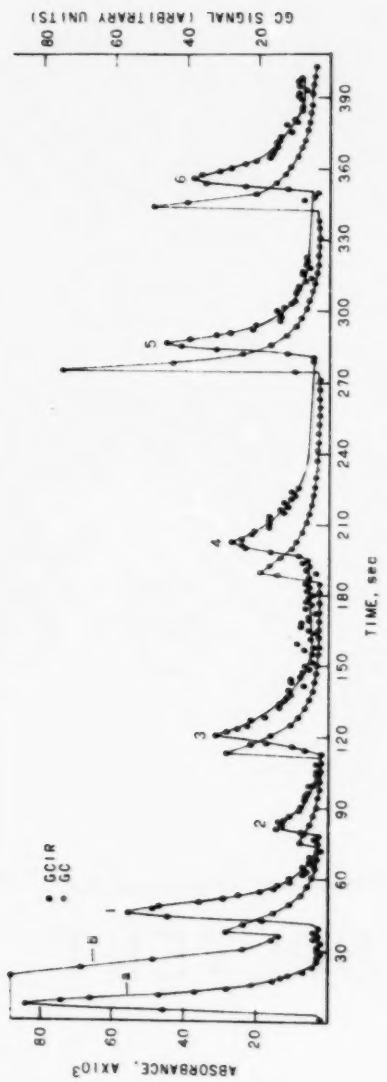

Figure 15. (a) The reconstructed chromatogram from IR absorbance data and

(b) The original chromatogram

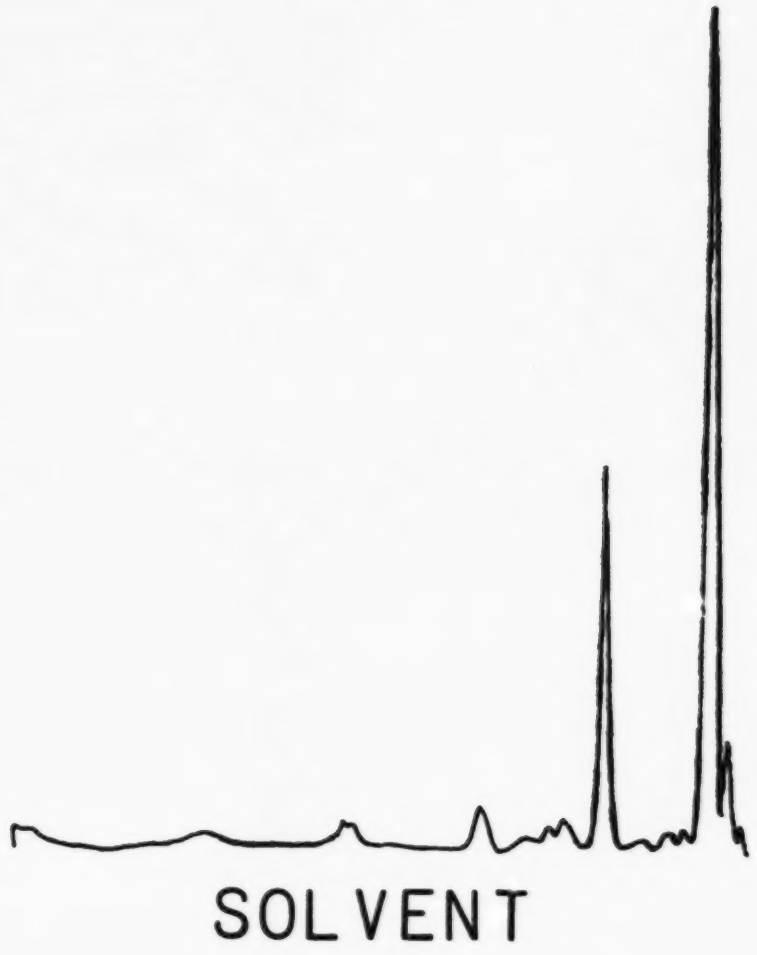

Figure 16. Single scan spectra of the eluates in Fig. 15
(a) Chloroform (solvent peak)

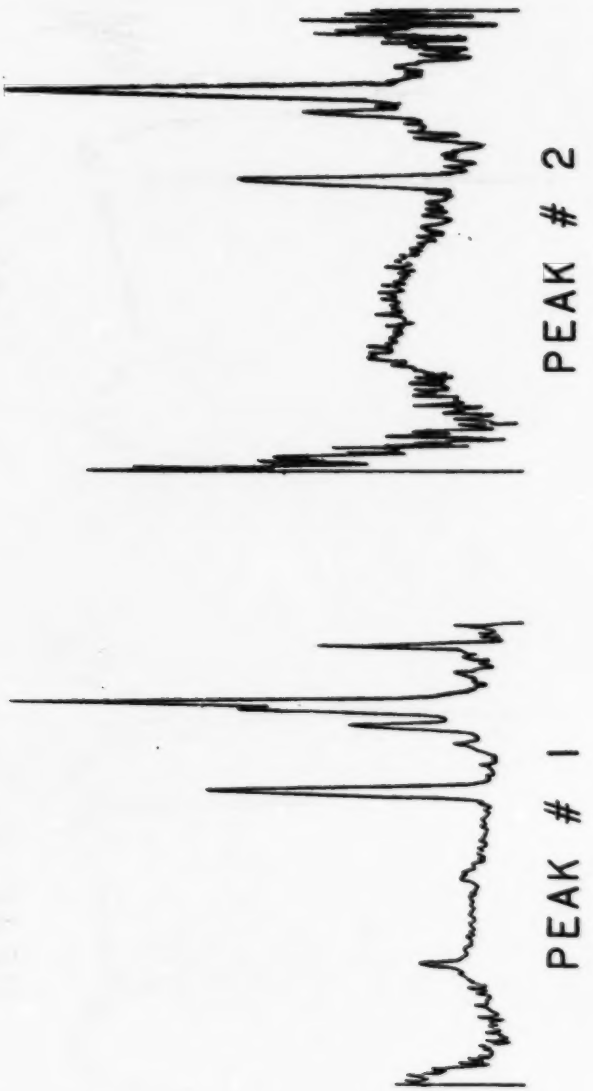

Figure 16. Single scan spectra of the eluates in Fig. 15
(b) Dimethyloxalate (peak #1) and the impurity in the Dimethyloxalate reagent (peak #2)

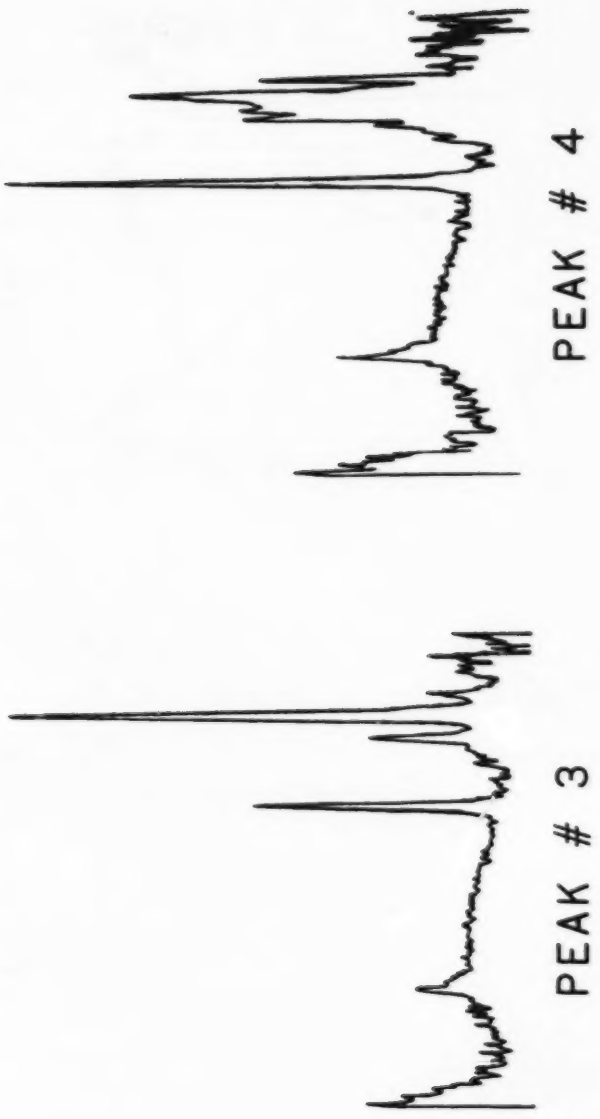

Figure 16. Single scan spectra of the eluates in Fig. 15
(c) Diethyloxalate (peak #3) and Diethylmalonate (peak #4)

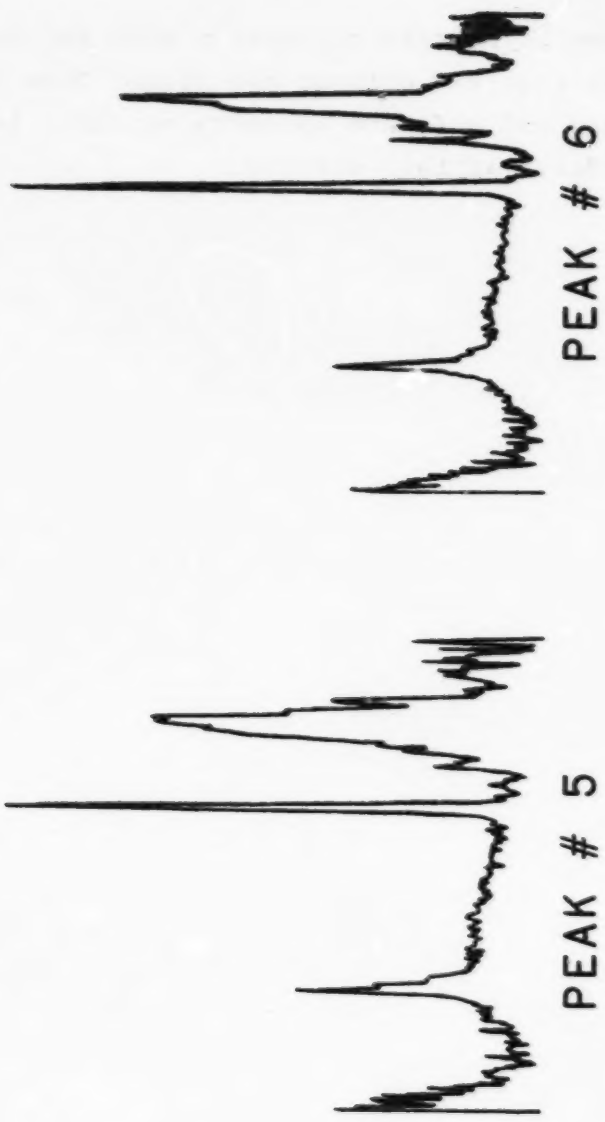

Figure 16. Single scan spectra of the eluates in Fig. 15
(d) Diethylethylmalonate (peak #5) and dimethyladipate (peak #6)

synchronizing GC/IR data collection with the GC operation is required without the signal from the FID. Both hardware and software to carry out this improvement had been ordered at this writing.

SECTION VI

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